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Stimuli response of polysoap hydrogels in aqueous solution and DC electric fields[☆]

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Abstract

Novel types of polysoap hydrogels based on hydrophobically-modified polyelectrolytes crosslinked with *N,N*-methylenebisacrylamide have been prepared by free radical polymerization at 70–80°C in aqueous solution with ammonium persulfate as initiator. Poly(diallylamine-co-*N,N*-dodecylmethyldiallylammonium bromide) (PDA-C12), poly(*N*-methyldiallyl-co-*N,N*-dodecylmethyldiallylammonium bromide) (PMDA-C12) both contain hydrophobic side chains with 12 carbon atoms. The swelling behavior of these polysoap hydrogels was studied by immersion of the gels in buffered solutions at various pHs and ionic strengths. It was found that the structure of the polysoap backbone influenced the pH-dependent swelling and deswelling. The swelling process is reversible after repeating cycles of swelling and deswelling induced by a change of pH in appropriate buffer solutions. SEM micrographs of polysoap gels indicate that the network structures are characterized by the presence of large open pores or small closed pores. The stimuli response of the polysoap gels in electric fields was also investigated. In a contact electric field, deswelling was observed at the anode side of the gels. In a non-contact electric field, the gels bend towards the anode. The gels can turn back to the original shape and bend toward the cathode with time when higher electric potentials are applied. These properties of the gels are related to both the change of osmotic pressure caused by mobile ions and by hydrophobic interactions. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: pH-sensitive polysoap hydrogels; (De)swelling behavior; Ionic strength; DC electric field; Bending angle

1. Introduction

Cross-linked polyelectrolytes are usually ionic strength and pH sensitive polymers because their structures contain both charges and ionizable groups [1,2]. In general, these polymer gels also exhibit stimuli-responses induced by electric fields, such as, swelling/deswelling, shape change, etc. These properties can be utilized for actuators [3]

[☆] This paper is dedicated to Professor T. Kunitake on the occasion of his official retirement from academia.

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and electromechanical engines (energy conversion) [4,5].

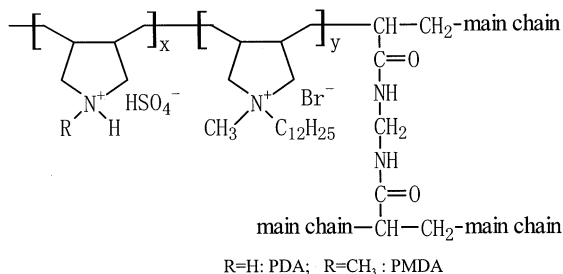
Polysoaps are hydrophobically-modified polyelectrolytes containing both hydrophilic and hydrophobic groups attached to the polymer main chains. Polysoap hydrogels can be prepared by using crosslinkers during the polymerization process. Similar to the intelligent hydrogels which have been frequently discussed during the past decade, [6] polysoap hydrogels also exhibit environmental sensitivity. In general, the pH-sensitivity of hydrogels depend on ionizable acidic or basic pendent groups, such as carboxylic, amino and ammonium groups [7]. Recently much research has been and is being performed aimed at application of these hydrogels in drug delivery systems [8]. Particularly, polysoap gels can more easily bind to bioactive molecules, compared with normal gels due to the presence of their hydrophobic side chains. The conjugation and release of drugs with either high molecular weight or low molecular weight or of other bioactive molecules depend mainly on the hydrophilic–hydrophobic balance in the network structure of the gels [1].

Extensive experimental studies of the pH dependence of hydrogels have usually been focused on acrylamide derivatives that introduce charged groups at low concentrations in their polymer network. Poly(*N,N*-diethylacrylamide), [9,10] poly(*N*-isopropylacrylamide) [11,12], partially-hydrolyzed polyacrylamide and their copolymers [13], poly(methacrylic acid) [14], poly(*N*-acryloylpyrrolidine) [15] have all been found to show large volume changes in response to external stim-

uli, e.g. pH, temperature and electric fields. The kinetic behavior of these hydrogels has also been examined theoretically. [16,17] Generally, these hydrogels possess dominant hydrophilic characteristics, although some hydrogels contained short hydrophobic alkyl chains. Little attention has been paid to studies of polysoap hydrogels.

The mechanism of the stimuli-response of the gels in DC electric fields has been discussed frequently, but is still controversial. Grimshaw et al. [18] applied an electrodiffusion theory to explain the swelling pattern of a poly(methacrylic acid) gel. De Rossi et al. [3] explained the anisotropic deswelling of poly(vinyl alcohol)/ poly(acrylic acid) membranes at the anode by the local pH decrease associated with water electrolysis. Kim et al. [19] adopted a theory involving depletion polarization to explain gel bending in a DC electric field. Tanaka et al. [20] reported anisotropic contraction of negatively charged gels when electrodes were in contact with the gels. This gel contraction was accounted for by the electrophoretic migration of the negatively charged gels toward the anode.

Based on our previous studies of polysoaps, [21–25] we have synthesized two types of novel polysoap hydrogels: cross-linked random poly(*N*-methylallylamine-co-*N,N*-methyl dodecylallylammmonium bromide) and cross-linked random poly(diallylamine - co - *N,N* - methyl dodecylallylammmonium bromide). These polysoap hydrogels contain extended hydrophobic side chains with 12 carbon atoms (Scheme 1). Herein, we report the swelling and deswelling of these gels in buffered solutions as a function of pH and ionic strength and the stimuli response of the gels in DC electric fields. Furthermore, their network structures were examined by electron microscopic techniques. The results reveal that the pH response is not only determined the electrostatic effects but that hydrophobic interactions also play an important role. The gels exhibited deswelling at the anode side in contact DC electric fields and shape changes in non-contact DC electric fields. These characteristics are enhanced by an increase of the applied electric potential.



Scheme 1. Schematic illustration of structures of polysoap gels.

2. Experimental

2.1. Materials

N-methyldiallylamine and *N,N*-methyldodecyl-diallylammmonium bromide were synthesized according to the literature [25]. Sulfuric acid (95–97 wt%, Merck), *N,N*-methylenebisacrylamide (Serva), ammonium persulfate (Acros) and DMSO (Aldrich) were used as received. Diallylamine (Acros) was distilled before use. Aqueous HCl solutions (30%, Boom B.V.), NaBr (UCB), citric acid (Merck), phosphoric acid (Merck) and boric acid (Merck) were used as received.

2.2. Synthesis

Two sets of polysoap hydrogels were prepared by free-radical polymerization.

2.2.1. Crosslinked random poly(*N*-methyl-diallylamine-co-*N,N*-methyldodecyl-diallyl-ammonium bromide) with 3 wt% of crosslinker (designated as *PMDA-C12* (c.l.3%) gel)

The gel was prepared according to the following procedure: 4.537 g (0.056 mol) of *N*-methyldiallylamine was dissolved in 8.3 g of distilled water in a 50 ml flask and 2.09 g (0.0204 mol) of sulfuric acid (95–97 wt%) was added dropwise under stirring at room temperature. The solution was stirred for 1 h at room temperature. Subsequently 1.64 g (0.0046 mol) of *N,N*-methyldodecyl-diallylammmonium bromide, 0.248 g (3 wt%) of *N,N*-methylenebisacrylamide as a crosslinker and 0.085 g (1 wt%) of ammonium persulfate as an initiator were added.

The mixture was bubbled for at least 30 min with dried nitrogen gas to remove oxygen and the solution was quickly injected using a syringe into the cavity between two glass plates using a silicon rubber gasket (2 mm diameter) as a spacer and clips for fixing glass plates. The glass plates (100 × 100 × 3 mm) were coated with a thin layer of silicone oil before use. The assembly was then kept in an oven at 70–80°C for 3 days. After polymerization, the hydrogels were removed from the model and soaked in 500 ml deionized water

for 1 week to extract unreacted compounds. The water was replaced daily.

2.2.2. Crosslinked random poly(diallylamine-co-*N,N*-methyldodecyl-diallylammmonium bromide) (designated as *PDA-C12* (c.l.3%) gel.)

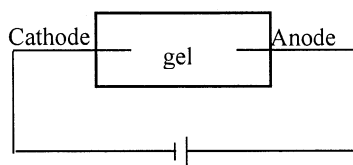
The gel was prepared according to the following procedure: 5.0 g (0.051 mol) of diallylamine was dissolved in 6.4 g of distilled water in a 50 ml flask and 2.58 g (0.026 mol) of sulfuric acid (95–97 wt%) was added dropwise under stirring at room temperature. The solution was stirred for 1 h at room temperature. 2.06 g (0.0057 mol) of *N,N*-methyldodecyl-diallylammmonium bromide, 0.29 g (3 wt%) of *N,N*-methylenebisacrylamide as a crosslinker and 0.09 g (1 wt%) of ammonium persulfate as an initiator were added. Polymerization was carried out using a similar procedure as given above.

2.2.3. Swelling experiments

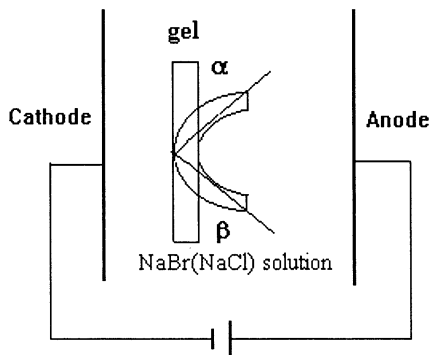
Polysoap hydrogels were equilibrated in deionized water for at least 1 week and then cut into rectangularly shaped plates (about 10 × 10 × 5 mm). The hydrogels were dried for 1 day and then for 8 h under vacuum at room temperature. A simulated physiological buffer solution [26] was made by dissolving 7 g of citric acid monohydrate, 3.83 g of phosphoric acid (85 wt%) solution and 3.54 g of boric acid in 343 ml of a 1 M NaOH solution. This solution was mixed with deionized water to obtain 1 l of a stock solution. Buffer solutions with pH values of 2, 4, 6, 8, 10 and 12 were prepared by adding 30 wt% HCl solution.

The dried gels were soaked separately in 50 ml of the buffer solution of pH 2, 4, 6, 8, 10 and 12, respectively, for 2 days with fresh solutions being replaced daily. The gels were withdrawn from the buffer solution and weighted after removal of excess surface water by light blotting with laboratory tissue. Excellent reproducibility in swelling values was obtained for each sample with a relative standard error of 1% or less. The swelling ratio of the gels was defined as:

$$\text{Swelling ratio} = \frac{W_s - W_d}{W_s} \times 100\%$$



Scheme 2. Schematic illustration of deswelling measurements under the contact DC fields.



Scheme 3. Schematic illustration of bending measurements under the non-contact DC field.

where W_s is the weight of the swollen gel and W_d is the weight of the dried gel.

Deswelling kinetics and reversibility of swelling in buffers with different pH were examined as follows. The gels equilibrated in deionized water were soaked into 50 ml of buffer solution with a pH of 12. Sample weights were taken once every 30 min until equilibrium of deswelling was reached (about 2 h). The samples were withdrawn from the buffer solution and immediately soaked into another buffer solution with a pH value of 8. The sample weights were taken every 30 min until equilibrium of swelling was reached (about 3 h).

Swelling measurements at different ionic strengths were performed by soaking the dried gels separately in 50 ml of 0.001, 0.01, 0.05, 0.1 and 1 M NaBr solutions for 2 days with fresh solutions being replaced daily. The measurements were carried out as described above.

2.2.4. Electron microscopy

Samples were equilibrated in deionized water for at least 1 week and frozen at -180°C (liquid nitrogen) and then freeze dried. SEM was per-

formed using a JEOL 6320 F field emission microscope with an acceleration voltage of 2 KV. The probe current was 1×10^{-10} A.

2.2.5. Deswelling measurements in contact DC electric fields

Scheme 2 shows schematically the set-up for deswelling measurements in contact DC electric field. The gels, pre-equilibrated and swollen in deionized water, were cut into rectangular shaped plates (about $10 \times 10 \times 5$ mm) and weighted. Two platinum wires (ϕ 2.5 mm) were inserted into the gel sample. The distance between the two electrodes was about 5 mm. When an electric stimulus was applied, water was released from the gel at the anode side. The water seeping from the gel was removed by light blotting with laboratory tissue till the end of experiment. Finally, the deswollen gels were weighted again. The deswelling ratio was expressed in terms of the retained weight ratio Rw :

$$Rw = \frac{W_{\text{after}}}{W_{\text{before}}} \times 100\%$$

where W_{after} is the weight of the gel after deswelling and W_{before} is the weight of the gel before deswelling.

2.2.6. Bending angle measurements in non-contact DC electric fields

Scheme 3 shows schematically the technique for the bending angle measurements in the non-contact DC electric field. Aqueous solutions (0.004 mol l^{-1} of NaBr) were poured into an organic glass case equipped with two parallel platinum electrodes (ϕ 2.5 mm). The separation between the electrodes was about 30 mm. The swollen gels, pre-equilibrated in deionized water, were cut into rectangular columns (about $30 \times 10 \times 5$ mm) and were placed in the center of the case. A white paper-drawn scale in angle degree was placed outside of the case bottom. When an electric stimulus was applied, the degrees of bending were measured by reading the deviated angle from the vertical position. Due to the different bending of both sides of gel, the bending angle θ was defined as:

$$\theta = \alpha + \beta$$

3. Results and discussion

The structures of the new polysoap hydrogels are shown in Scheme 1. Obviously, the structure of the polymer main chain affects the pH sensitivity because of the presence of the amino groups. The equilibrium degrees of swelling, defined as the weight percentage of water in the swollen state at different pH values, are shown in Fig. 1. Generally, the two types of polysoap hydrogels have a

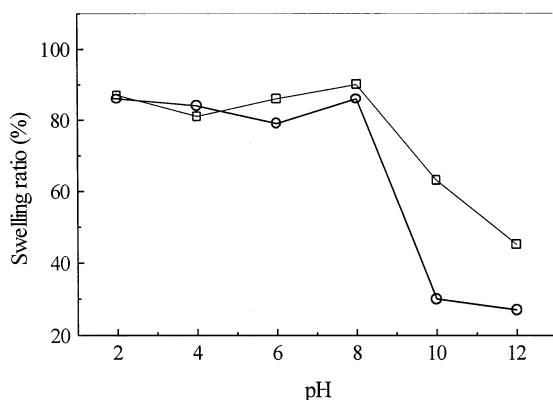


Fig. 1. The swelling ratio of polysoap gels at different pH values in buffer solutions. \square : PDA-C12(c.l.3%); \circ : PMDA-C12(c.l.3%).

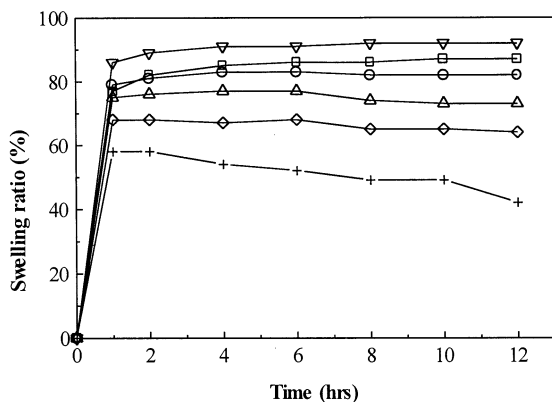


Fig. 2. Kinetic swelling curves for the PDA-C12(c.l.3%) gel at different pH values in buffer solutions. \square : pH 2; \circ : pH 4; \triangle : pH 6; ∇ : pH 8; \diamond : pH 10; $+$: pH 12.

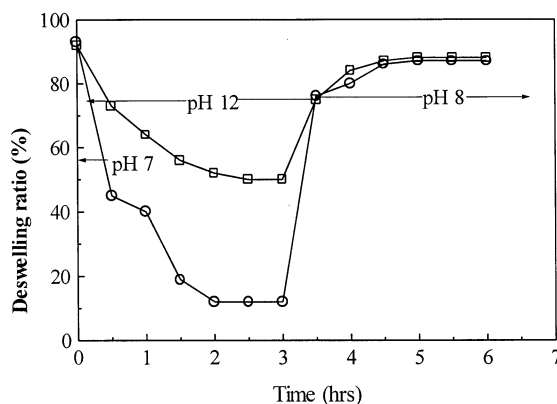


Fig. 3. Kinetic swelling and deswelling curves for polysoap gels at pH 12 and pH 8 in buffer solutions. \square : PDA-C12(c.l.3%); \circ : PMDA-C12(c.l.3%).

higher degree of swelling at acidic pH. This is attributed to protonation of the amino groups in the network in the acidic medium, resulting in increased repulsion between the charged groups in the network and concomitant expansion. As anticipated, the swelling ratio of PMDA-C12(c.l.3%) and PDA-C12(c.l.3%) decreases rapidly at pH > 8, particularly for PMDA-C12(c.l.3%). Interestingly, only difference between the structures of both the gels is the additional presence of methyl groups in PMDA-C12(c.l.3%) which causes quite different swelling behavior. This behavior can be ascribed to a sharp transition from extended polymeric chains at pH < 8 to a compact, coiled globular morphology in basic media. Fig. 2 illustrates the dynamic swelling expressed as the swelling ratio as a function of the time after immersion of gels in buffered solutions at different pH values in the range of 2–12. It is clear that the anhydrous specimens rapidly absorb the aqueous medium. A noticeable increase of the swelling ratio is observed within the first 2 h. The time necessary to reach the equilibrium swelling seems to be independent of the pH of the buffered solution.

Fig. 3 illustrates pH-dependent swelling and deswelling of the polysoap hydrogels. When the polysoap hydrogels were equilibrium-swollen in a buffer solution at pH 7 and subsequently trans-

ferred to a buffer solution of pH 12, the swelling ratio rapidly decreased from ca. 95% for pH 7 to ca. 10% for pH 12. Obviously, the hydrogels undergo an abrupt change from the semi-transparent swollen state to an opaque deswollen solid state. Subsequently, when these gels were placed in a buffer solution of pH 8, they rapidly swell again. We conclude that the swelling is reversible. We contend that the sharp transition of swelling/deswelling for PMDA-C12(c.1.3%) finds its origin in both electrostatic effects and hydrophobic intermolecular aggregation. This polysoap is more hydrophobic than PDA-C12(c.1.3%) and exhibits much more pronounced (de)swelling behavior.

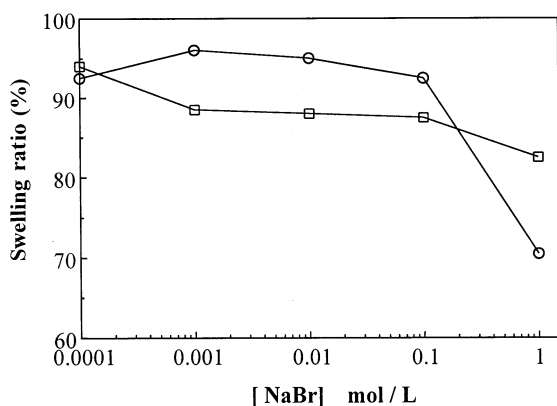


Fig. 4. The swelling ratio of polysoap gels in aqueous solutions as a function of ionic strength. \square :PDA-C12(c.1.3%); \circ :PMDA-C12 (c.1.3%).

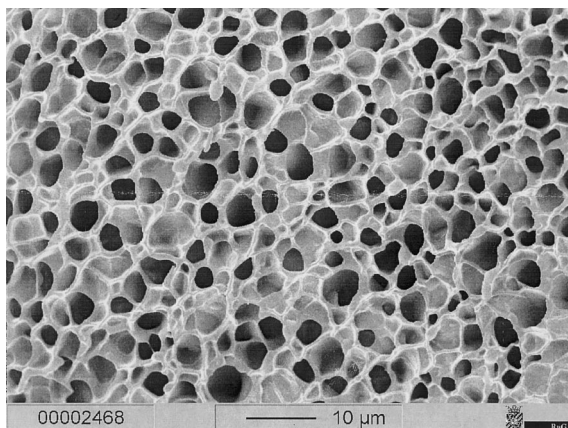


Fig. 5. SEM micrograph of PDA-C12(c.1.3%) gel.

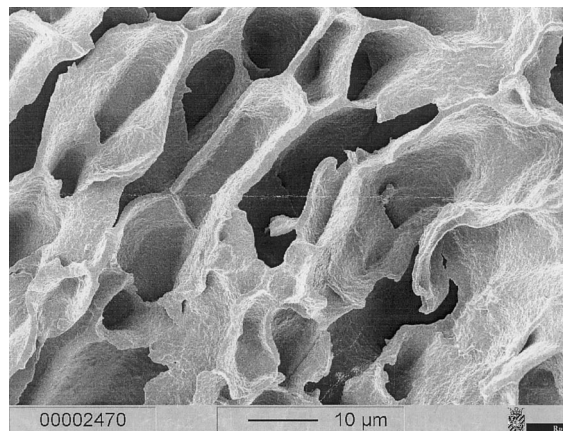


Fig. 6. SEM micrograph of PMDA-C12(c.1.3%) gel.

The main mechanism of hydrophobic aggregation is the release of water from hydrophobic hydration spheres [27]. Probably, the formation of different aggregated network structures plays an important role which is also reflected in Figs. 5 and 6 (vide infra).

The effect of ionic strength on the equilibrium swelling was studied for the two types of polysoap hydrogels. Fig. 4 shows the swelling ratio of polysoap hydrogels in aqueous NaBr solutions at room temperature. It is shown that, the swelling ratio decreases rapidly, mainly for PMDA-C12(c.1.3%), at higher electrolyte concentrations (above 0.1 mol). Generally, the swelling ratio of polyelectrolyte gels depends on the association state of ionic groups within the polymer and on the affinity of hydrogels for water [2]. In the case of polysoap hydrogels, hydrophobic interactions probably also play an important role. PMDA-C12(c.1.3%) and PMDA-C12(c.1.3%) possess the same ionic group and the dissociation characteristics of this ionic group are considered to be similar for both gels. However, PMDA-C12(c.1.3%) is more hydrophobic than PDA-C12(c.1.3%). If the gel is more hydrophilic, a repulsive force acts between the segments of the gels. On the other hand, according to the Donnan osmotic pressure equilibrium [28], an increase of movable counterions in solution leads to a decrease of osmotic pressure within the gel and causes shrinkage of the gel.

Figs. 5 and 6 show SEM micrographs of the network structures of PDA-C12(c.1.3%) and PMDA-C12(c.1.3%), respectively. The results clearly indicate that two different network structures are formed. At the same magnification, PDA-C12(c.1.3%) exhibits small closed micropores whereas PMDA-C12(c.1.3%) shows large open micropores. The micropore size is probably related to kinetic behavior of swelling and deswelling. Therefore, the difference in micropores will be related to the fact that PMDA-C12(c.1.3%) is more pH sensitive than PDA-C12(c.1.3%). Kaneko and co-workers [29] reported that hydrophilic gels like comb-type grafted poly(*N*-iso-

propylacrylamide) form ‘surface skin’ layers, entrapping water inside the gel upon the deswelling. Obviously, large, open micropores can hardly form such surface skin layers.

The stimuli response of the cationic gels in electric fields was studied by two experimental methods involving contacting and non-contacting electrodes with gels. In the first type of experiment the electric current was conducted through the gels, while in the second experiment the current was passed through the surrounding salt solution.

Fig. 7 shows the deswelling behavior of the polysoap gels as a function of the applied electric potential in contact DC electric fields. Significant deswelling at the anode side was observed. When an electric field was applied to the polyelectrolyte gels, deswelling usually occurred at the anode side. This phenomenon may be attributed to the local pH changes by the electrode reactions. At the same time, the gels undergo a change from a semi-transparent swollen state to an opaque deswollen solid state. The extent of deswelling was dependent on the intensity of the applied electric field and interestingly, the tendency of deswelling followed the order of hydrophobicity: PMDA-C12(c.1.3%) > PDA-C12(c.1.3%).

Fig. 8 indicates that the time necessary to reach the equilibrium deswelling is about 20 min, and the difference of retained weight ratio seems to coincide with the regularities in Fig. 7. Although theories, such as electrodiffusion, electrophoresis, electro-osmosis and local pH profiles caused by water electrolysis can explain the mechanism of stimuli-response in DC electric fields for normal polyelectrolyte gels, this analysis may not be adequate for explaining the effect of hydrophobicity in the case of the polysoap gels. Presumably, hydrophobic interaction may well be one of the driving forces for deswelling. On the other hand, polysoap gels can hardly form ‘surface skin’ layers [19,29] due to the flexibility of the hydrophobic side chains.

Fig. 9 shows the bending toward the anode for polysoap gels in the applied non-contact electric fields. The two types of polysoap gels show bending of both ends of the gel towards the anode. Fig. 10 shows the maximum bending angle as a function of the applied electric potential differ-

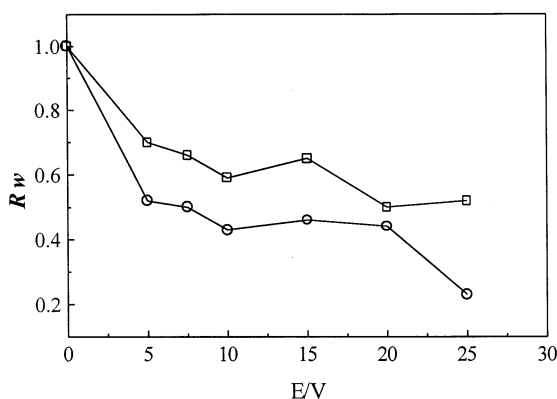


Fig. 7. Retained water ratio for polysoap gels as a function of voltage in the contact DC fields. □:PDA-C12 (c.1.3%); ○:PMDA-C12 (c.1.3%).

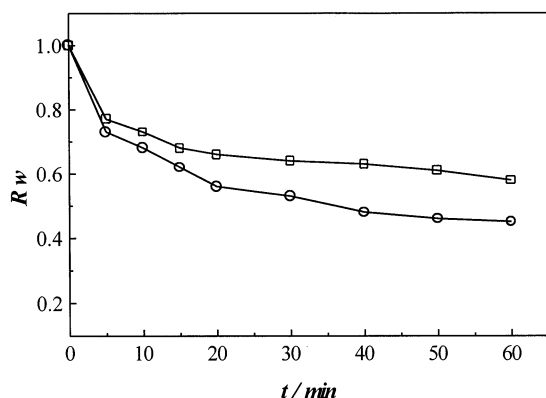


Fig. 8. Retained weight ratio-time curves for polysoap gels in the contact DC fields(10V). □:PDA-C12 (c.1.3%); ○:PMDA-C12 (c.1.3%).

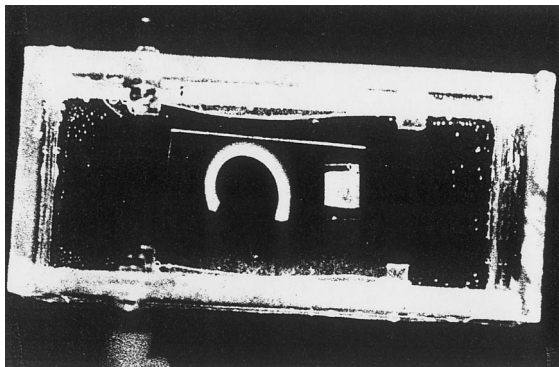


Fig. 9. The bending motion of polysoap gels in the non-contact DC fields.

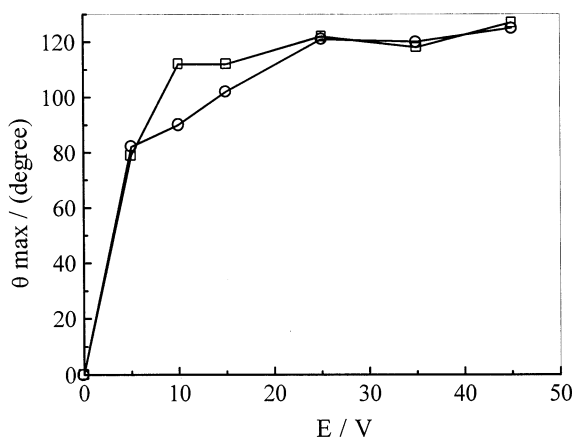


Fig. 10. The dependence of bending angle on voltage in the non-contact DC fields. \square :PDA-C12 (c.1.3%); \circ :PMDA-C12 (c.1.3%).

ence. Obviously, the bending angle is proportional to the electric potential difference. As shown in Fig. 11, the degree of bending towards the anode increases with time for a given electric potential difference (15 V). The mechanism of the shape change of the gels is usually explained in terms of Flory's theory of osmotic pressure. When a DC electric field is applied, mobile ions (Br^-) move toward their counter electrode, the anode. As a result, an ion concentration gradient is set up. Consequently, the osmotic pressure associated with this ion concentration difference between the inside and the outside of the gel will be changed. Shiga and co-workers [30] reported detailed calcu-

lations for this process. When the osmotic pressure facing the cathode increases with anions moving towards the anode, the gel facing the cathode swells, which results in bending toward the anode. But it deswells when the osmotic pressure decreases. This indicates that bending is one of the mechanisms accompanying (de)swelling. The bending towards the anode is consistent with deswelling at the anode side and increased swelling at the cathode side.

Interestingly, as shown in Fig. 12, PDA-C12 turns back to its original shape and even bends towards the cathode as a function of time at a

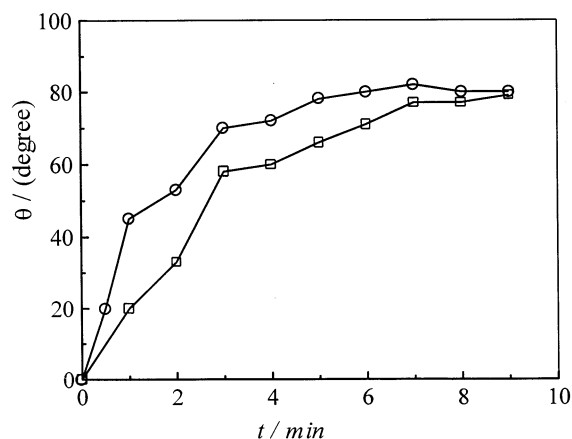


Fig. 11. The bending angle-time curves in the non-contact DC fields (15V). \square :PDA-C12 (c.1.3%); \circ :PMDA-C12 (c.1.3%).

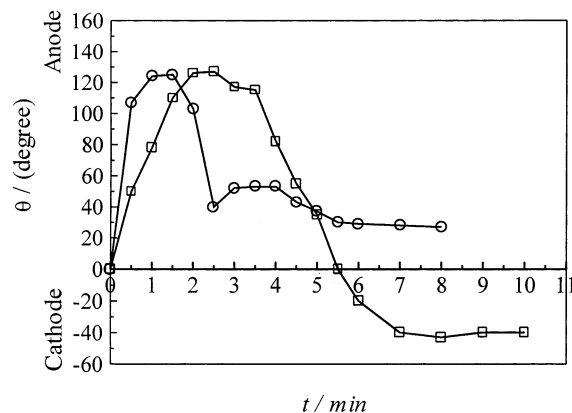


Fig. 12. The shape changing recovery and bending toward the cathode with the length of time in the non-contact DC fields (45V). \square :PDA-C12 (c.1.3%); \circ :PMDA-C12 (c.1.3%).

higher potential difference (45 V). PMDA-C12 also show this tendency of turning back, but this occurs significantly slower than for PDA-C12. This phenomenon is hardly observed for a lower potential difference. For the present experiments, cations (quaternary ammonium) are immovable ions. When the maximum bending was reached, anions move toward the anode side resulting in a decrease of the halide ion concentration at the cathode side. To maintain electrical neutrality, Br^- ions from the solution move into the gel due to the permselectivity of the gel to anions. In the applied electric field this will result in an increase of the anion concentration in the gel facing the cathode. As a result, deswelling at the cathode side occurs. When a higher potential difference is applied, more water will be electrolyzed. Therefore, the reverse bending will be enhanced by OH^- migration in the gel. In the present experiments, the anions move faster in PDA-C12 gels than in the other gels. This may be the reason for the faster recovery and bending towards the cathode in the case of PDA-C12. This difference may be related to the fact that PDA-C12 is more hydrophilic than PMDA-C12 carrying the additional methyl groups.

4. Conclusions

The pH-dependent swelling/deswelling behavior of polysoap hydrogels was examined for different polysoap hydrogels at varying ionic strengths. The results can be rationalized by taking into account both electrostatic and hydrophobic interactions. PMDA-C12 undergoes rapid deswelling at pH 12 due to its enhanced hydrophobic nature and the formation of large, open micropores.

The stimuli response of polysoap gels in applied electric fields has been investigated through measurements of deswelling and bending angles. The gels exhibited considerable sensitivity both in the contact and non-contact electric field. In the contact electric field, the deswelling of the gels at the anode side depends on the field intensity. In the non-contact electric field, the gel bends towards the anode. When a higher potential difference was applied, the bent gels can be recovered to their

original shape and ultimately bend to the cathode. A mechanism might involve changes of the osmotic pressure caused by the difference in ion concentration between the inside and the outside of the gel. Hydrophobic interactions also appear to play an important role.

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